

1 **Chemocatalysis of sugars to produce lactic acid derivatives on**  
2 **zeolitic imidazolate frameworks**

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1 **Abstract**

2       Several research studies related to biorefining have focused on developing routes  
3 for biomass conversion into biomaterials or platform molecules. In this work, the ZIFs  
4 (zeolitic imidazolate frameworks) ZIF-8 and ZIF-67 have been tested as catalysts in the  
5 conversion of sugars (sucrose, glucose and fructose) into methyl lactate. ZIF-8 and ZIF-  
6 67 have the same sodalite type zeolite structure but behaved differently in the sugar  
7 conversion in methanol due to the respective presence of Zn and Co in their structures.  
8 ZIF-8 has been found to be the most active for the conversion of sugars into methyl  
9 lactate (yield 42%) and was reused in four catalytic cycles. The chemical and physical  
10 effects caused by these cycles on the catalysts have been studied by several techniques  
11 (X-ray diffraction, thermogravimetric analyses, infrared spectroscopy, X-ray  
12 photoelectron spectroscopy, scanning electronic microscopy and nitrogen adsorption).

13 **Keywords**

14 Biomass, MOF catalysis, Zeolitic imidazolate framework, Sugar conversion, Lactic acid

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## 1 **1. Introduction**

2        There is a growing interest in the development of new technologies based on  
3 biomass due to the depletion of fossil fuels and the high energy and chemical  
4 consumption worldwide. The concept of biorefining has emerged as an example of the  
5 integrated production of fuels (biofuels), heat and electricity (biopower) and  
6 biomaterials [1-4]. One of the platform molecules produced from biomass is lactic acid  
7 [5], which is the most important hydroxycarboxylic acid due to its wide range of  
8 applications in the cosmetics, pharmaceutical and chemical industries [6,7]. Above all,  
9 the main use of this compound is in the polymer market, since lactic acid is the  
10 precursor for a biodegradable polymer called polylactic acid [8,9] that could substitute  
11 polystyrene or polyethylene terephthalate [5].

12        Over 90 % of commercial lactic acid is produced by a biotechnological route [5],  
13 the fermentation of aqueous glucose, but this process has some drawbacks such as a  
14 long reaction time because of its low reaction rates, high energy consumption and large  
15 amount of waste produced in the neutralization and purification steps [10].

16        Firstly, homogenous catalysis was studied as an alternative, and various industrial  
17 routes from petrochemical resources, such as acetaldehyde, have been used for lactic  
18 acid production [11]. Some research studies have reported the use of homogenous  
19 catalyst in the production of lactic acid [12,13]. For instance, Zhou et al. [12] developed  
20 a method for the conversion of carbohydrates into methyl lactate using  $\text{SnCl}_4$  as catalyst  
21 with inorganic bases. The authors used NaOH to neutralize the protons generated in the  
22 methanolysis of  $\text{SnCl}_4$ , increasing the yield to methyl lactate. However, the used  
23 catalysts are toxic and corrosive and their recovery is difficult, so this route is not an  
24 attractive alternative.

1           Recent research has focused on heterogeneous catalysis where the catalysts could  
2 be recovered and reused with low cost. The challenge is to find an efficient catalyst to  
3 produce lactic acid from biomass. Over the past few years, several solid catalysts have  
4 been applied for the conversion of sugars. Different zeolites were used for this purpose  
5 such as BEA-type zeolite [14-16], MFI-type zeolite [17] and FAU-type zeolite [18,19].  
6 A few mesoporous materials, such as Sn-MCM-41 [17,20-22] and SBA-15 [17] were  
7 also studied with good results. In addition, other kinds of solids such as tin-exchanged  
8 montmorillonite clay [23], supported noble metal catalysts [24], alumina supported  
9 KOH [25] and simple carbon-silica composite [26] were tested in this reaction.

10           Catalytic lactic acid production using sugars has a complex mechanism (see  
11 reaction pathway in Fig. S1) where several stages are involved. Lewis acid sites play an  
12 essential role in retro-aldol reaction, isomerization and 1,2-hydride shift; and Brønsted  
13 acidity is important in hydrolysis and dehydration [27]. It should be pointed out that  
14 direct obtaining of methyl lactate has some advantages in front of lactic acid, due to the  
15 fact than an esterification step and a hydrolysis stage are need for lactic acid purification  
16 [5]. Besides methyl lactate is a lactic acid precursor, it has its own applications such as  
17 green solvent.

18           Metal-organic frameworks (MOFs) are crystalline hybrid compounds formed by a  
19 metal cluster coordinated with organic linkers. These materials present a high porosity  
20 and an easy tunability of their pore size and shape and final functionality [28-31]. For  
21 these reasons, MOFs are considered as potential materials in several applications such  
22 as adsorption [32], gas separation and storage [33], membranes [34] and medicine [35].  
23 However, the most promising application of this family of materials is perhaps catalysis  
24 [36-42].

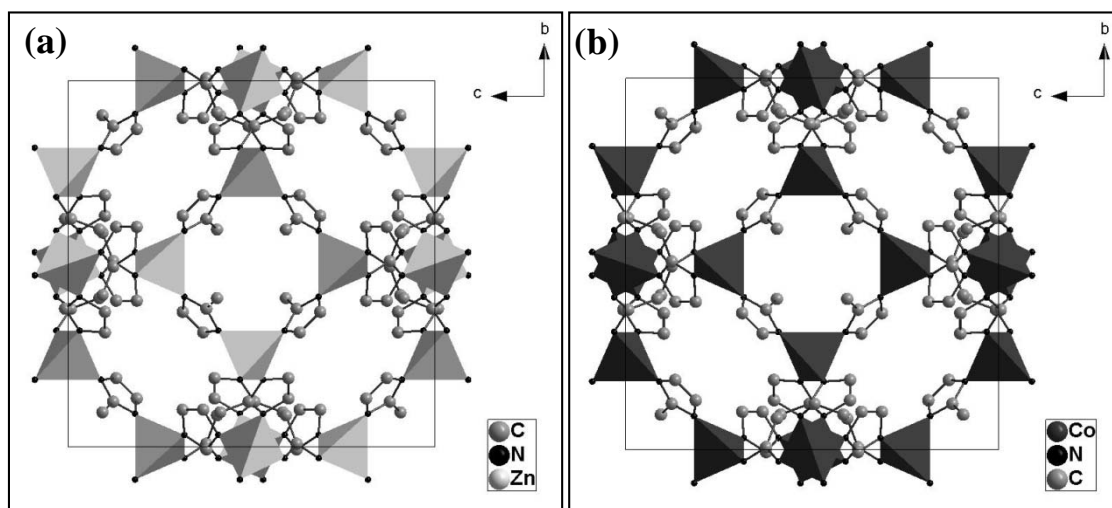
1           Within the context of MOFs, ZIFs (zeolitic imidazolate frameworks) are a  
2 subclass with zeolite-type topology [43]. ZIFs are well-known due to their high  
3 chemical and thermal stability, the ease of obtaining them, their high porosity and their  
4 3D porous and isotropic framework. Therefore, this class of compounds is very  
5 promising for a wide range of applications. ZIF-8 and ZIF-67, whose metal atoms are  
6 Zn and Co, respectively, both have sodalite type zeolitic topology [44,45]. Crystal  
7 structures of both solids are represented in Fig. 1. In ZIF-8,  $\text{ZnN}_4$  tetrahedra are linked  
8 by methylimidazolate ligands forming a 3D framework with large cavities of 11.6 Å  
9 accessible by small windows of 3.4 Å. On the other hand, the ZIF-67 framework, where  
10  $\text{CoN}_4$  tetrahedra are connected by imidazolate linkers, presents cavities of 11.4 Å and  
11 small windows of 3.3 Å [45]. Note that even though the pore apertures of the ZIFs are  
12 small, their flexibility induced by the organic linkers plays an important role. The  
13 microporous catalysts studied here have cavities large enough to accommodate the  
14 molecular diameters of glucose and fructose (ca. 8.5 Å) [46], as also occurred when  
15 encapsulating caffeine (6.1 x 7.6 Å) in ZIF-8 [47]. In addition, the so-called gate  
16 opening effect was also explained for ZIF-7 [48] when adsorbed guest species with size  
17 larger than that of the MOF aperture.

18           Given the characteristics of the ZIF-8 material, it is one of the most extensively  
19 studied ZIFs and has been tested as a heterogeneous catalyst for a number of reactions  
20 including the Knoevenagel reaction [49], transesterification [50], Friedel-Crafts  
21 acylation [51], monoglyceride synthesis [52], the formation of carbonates [53],  
22 hydrogen production [54] and multifunctional catalyst [55]. ZIF-67 has also been  
23 studied as a heterogeneous catalyst, with better performance in the formation of  
24 carbonates than ZIF-8 [56].

1        There are few publications concerning MOFs used as catalysts in biomass  
2 transformation. Cirujano et al. have recently reported the use of Zr-containing MOFs  
3 (UiO-66 and UiO-66-NH<sub>2</sub>) for the esterification of levulinic acid with some alcohols,  
4 obtaining high alkyl levulinates yields [57]. Other authors have functionalized MOFs  
5 for fructose conversion [58,59] and glucose isomerization [60].

6        Given that the use of solid acid catalysts for the conversion of sugars has become  
7 attractive for many researchers and there remains the challenge of finding new  
8 applications of MOFs, in this work we report on the use of ZIF-8 and ZIF-67 as  
9 catalysts in the transformation of sugars in methanol (sucrose, glucose and fructose) to  
10 methyl lactate. Both ZIFs could be interesting alternative materials in catalytic  
11 biorefinery for this new kind of processes.

12



13

14 **Fig. 1. Representation of ZIF-8 (a) and ZIF-67 (b) frameworks using Diamond 3.2 software. Crystal**  
15 **data from CCDC (The Cambridge Crystallographic Data Centre): ZIF-8 (CCDC code**  
16 **VELVOY)[44]; ZIF-67 (CCDC code GITTOT)[45].**

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18

## 1    **2. Experimental**

### 2    **2.1. Catalyst preparation**

3            ZIF-8 was synthesized using a previous method reported elsewhere [47]. The  
4 precursor solution had a molar ratio of  $\text{Zn}^{2+}$ :2-methylimidazole: $\text{H}_2\text{O}$ :MeOH =  
5 1:12:313:177. This solution was prepared as follows. Firstly, 3.15 g of 2-  
6 methylimidazole (99 % purity, Sigma-Aldrich) was dissolved in 20 mL of methanol  
7 (Multisolvent HPLC grade, Scharlau). Secondly, 0.95 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98 %  
8 grade, Sigma-Aldrich) was dissolved in 20 mL of methanol and 10 mL of deionized  
9 water. Each solution was stirred individually for 10 min after which the solution  
10 containing the metal was added to the linker solution. The mixture was maintained at  
11 room temperature under stirring for 2 h. Then the solution was centrifuged at 10,000  
12 rpm for 20 min. The solid product was washed with methanol twice and dried at 70 °C  
13 overnight.

14            The preparation method of ZIF-67 was the same, but changing the metal by using  
15 Co instead of Zn. In both cases, the same number of moles of metal was employed, so  
16 the molar ratio of the precursor solution was  $\text{Co}^{2+}$ :2-methylimidazole: $\text{H}_2\text{O}$ :MeOH =  
17 1:12:313:177. In this case, 0.93 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98 % grade, Sigma Aldrich) was  
18 used as the cobalt source.

### 19    **2.2. Catalytic reaction**

20            The sugar conversion to methyl lactate was carried out in a batch reactor, a 35 mL  
21 Teflon-lined stainless steel autoclave. Glucose (99 %, Alfa-Aesar), fructose (99 %, Alfa-Aesar)  
22 and sucrose (99 %, Fluka) were chosen as representative carbohydrates due  
23 to their low cost, simplicity and abundance.

1 The reaction was performed by dissolving 225 mg of carbohydrate in 8.0 g of  
2 methanol (Multisolvent HPLC grade, Scharlau). Besides, 30 mg of naphthalene (99 %,   
3 Sigma-Aldrich) was added as internal standard for subsequent quantification of the  
4 yields. The amount of catalyst added varied from 80 to 500 mg, but a normal batch was  
5 loaded with 160 mg of catalyst. The mixture with the sugar totally dissolved was  
6 transferred to a 45 mL Teflon-lined autoclave and the synthesis was carried out in an  
7 oven. The oven was heated in a ramp of 1 h up to the desired reaction temperature,  
8 varied from 80 to 160 °C. The reaction time starts when the reaction temperature is  
9 reached and it was varied between 1 and 48 h under rotating conditions (15 r.p.m, i.e.  
10 the whole autoclave rotates perpendicularly to its axial axis) (see in Fig. S2 the rotation  
11 inside the oven). 15 r.p.m. was chosen as rotation speed in the oven because it has been  
12 observed with ZIF-8 as catalyst that there were no apparent mass transfer limitations in  
13 the production of methyl lactate (i.e. no product yield increase, see Fig. S3).

14 Afterwards, the catalyst was recovered by centrifugation and the reaction liquid  
15 was analyzed by gas chromatography with a mass detector (GC-MS). The equipment  
16 was an Agilent 6850 GC system with a capillary column HP-5MS (30 m x 0.250 mm x  
17 0.25 µm) coupled with an Agilent 5975 MSD. The yields of the different products were  
18 calculated using the internal standard method and calibration curves using commercial  
19 compounds: methyl-S-(-)-lactate (98 %, Sigma-Aldrich), methylglyoxal 1,1-  
20 dimethylacetal (97 %, Sigma-Aldrich), also called pyruvaldehyde dimethyl acetal, and  
21 1,1,2,2-tetramethoxypropane (99 %, Sigma-Aldrich).

22 The determination of sugars was carried out using a commercial analytical  
23 method (Sucrose/Fructose/D-Glucose Assay Kit, Megazyme). The analysis was carried  
24 out as follows: firstly, the sugars samples were mixed with a solution which contains  
25 enzymes (different for each sugar), these enzymes transform sugars to glucose-6-



1 phosphate (G-6-P), and reaction lasts for a few minutes. Then another solution  
2 containing nicotinamide-adenine dinucleotide phosphate (NADP<sup>+</sup>) and enzyme  
3 glucose-6-phosphate dehydrogenase (G6P-DH) was added. In the presence of this  
4 enzyme, G-6-P is oxidized by NADP<sup>+</sup> producing its reduced form (NADPH), which is  
5 measured by increasing its absorbance at 340 nm using a UV-spectroscopy (V-670  
6 Jasco UV-vis spectrophotometer).

7 A series of experiments was carried out using sucrose as substrate with reused  
8 ZIF-8. The reaction conditions were 160 °C for 24 h with 160 mg of catalyst. Between  
9 each run, the recovered solid was dried under vacuum at 190 °C for 12 h, in order to  
10 remove adsorbed compounds.

### 11 **2.3. Catalyst characterization**

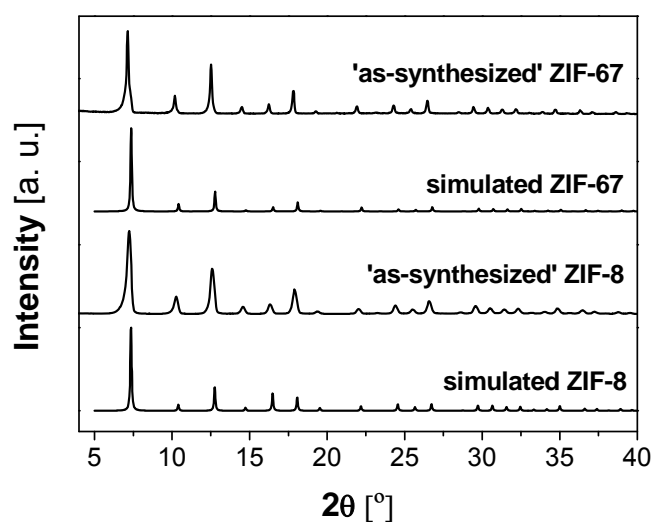
12 The diffraction patterns of the samples were measured by X-ray diffraction (XRD)  
13 using a D-Max Rigaku X-ray diffractometer with Cu-K $\alpha_1$  radiation ( $\lambda = 1.5418$ ) and a  
14 graphite monochromator. Thermogravimetric analyses (TGA) were carried out using  
15 Mettler Toledo TGA/SDTA 851e equipment. Samples were heated in air up to 850 °C  
16 with a heating rate of 10 °C/min. Scanning electronic microscopy (SEM) images were  
17 obtained over Pt-coated specimens using an Inspect F50 model scanning electron  
18 microscope (FEI). Nitrogen adsorption-desorption isotherms were obtained with a  
19 Micromeritics Tristar 3000. Previously, the samples were degassed at 190°C for 8 h  
20 under vacuum. Fourier transformed infrared spectra were measured on a Bruker Vertex  
21 70 FTIR with a deuterated triglycine sulfate (DTGS) detector and ATR Golden Gate  
22 accessory in the range 600-1,800 cm<sup>-1</sup>, with an accuracy of 4 cm<sup>-1</sup>. X-ray photoelectron  
23 spectroscopy (XPS) was performed with an Axis Ultra DLD (Kratos Tech.). The spectra  
24 were excited by a monochromatized Al K $\alpha$  source (1,486.6 eV) at 15 kV and 10 mA

1 and a pass energy of 20 eV was used for the individual peak regions. Binding energies  
2 were referenced to the internal standard C 1s (284.5 eV).

### 3 3. Results and discussion

#### 4 3.1. Catalyst characterization

5 The catalysts were characterized by different techniques in order to check their  
6 properties and stability. Fig. 2a shows a comparison of the experimental XRD patterns of  
7 as-synthesized materials (ZIF-8 and ZIF-67) with those simulated from their single crystal  
8 structures. There is a high degree of correspondence between the simulated and  
9 experimental patterns and they are in good agreement with those previously reported  
10 [44,45]. Both materials have the same crystalline framework corresponding to the  
11 sodalite structure and therefore their XRD patterns are similar. The wider peaks of ZIF-  
12 8 are consistent with a smaller particle size, as will be shown below.

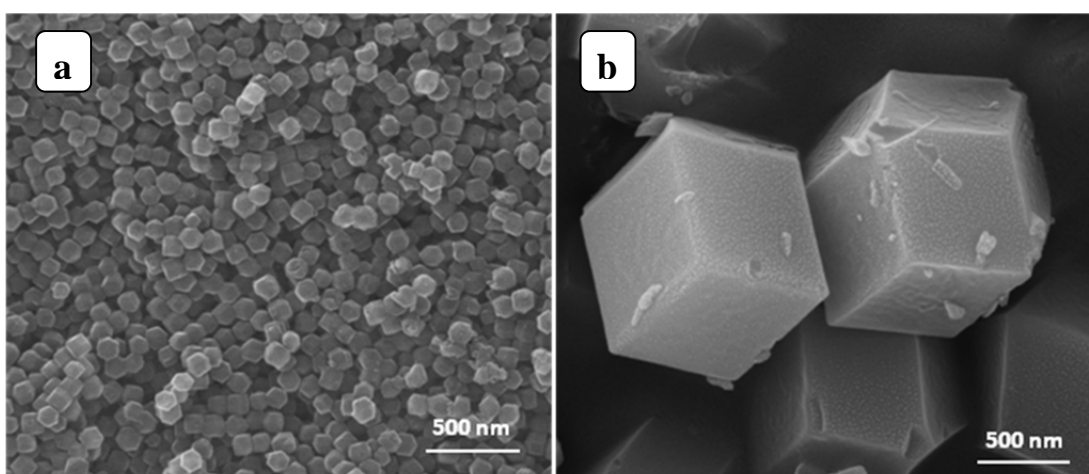


13  
14 **Fig. 2. XRD patterns of simulated ZIF-8, 'as-synthesized' ZIF-8, simulated ZIF-67 and 'as-**  
15 **synthesized' ZIF-67. Simulated XRD patterns are obtained from crystal structure data from**  
16 **CCDC.**

17

1 Thermogravimetric analyses (see Fig. 2S4) of the catalysts made in air show that  
2 ZIF-8 was thermally stable up to 450 °C, but ZIF-67 only up to 400 °C. This may be due  
3 to a stronger catalytic degradation in air of the metal Co present in ZIF-67, compared  
4 with the Zn in ZIF-8.

5 The size and morphology of the catalysts were studied by SEM. In Fig. 3a, ZIF-8  
6 crystals are observed with a rhombic dodecahedron shape and a 100-150 nm size, while  
7 Fig. 3b shows crystals of ZIF-67 with the same well-defined shape of around 1 μm size.  
8 The growth kinetics of ZIF-67 are faster than ZIF-8, so bigger crystals are formed,  
9 according to a previous report [61].



10  
11 **Fig. 3. SEM images of ZIF-8 (a) and ZIF-67 (b).**

12  
13 The textural properties, such as BET specific surface area and pore volume, of  
14 ZIF-8 and ZIF-67 were measured. The BET specific surface area is slightly larger for  
15 ZIF-67 ( $1,450 \text{ m}^2 \text{ g}^{-1}$ ) than for ZIF-8 ( $1,391 \text{ m}^2 \text{ g}^{-1}$ ). The same trend in pore volume is  
16 observed,  $0.69 \text{ cm}^3 \text{ g}^{-1}$  for ZIF-67 and  $0.66 \text{ cm}^3 \text{ g}^{-1}$  for ZIF-8. The similar textural  
17 properties for both materials are in agreement with their similar ZIF topology and with  
18 the similar cell volumes of  $4,905.2 \text{ \AA}^3$  (ZIF-8) [44] and  $4,877.5 \text{ \AA}^3$  (ZIF-67) [45].

### 3.2. Catalytic tests

The zeolitic-imidazolate frameworks (ZIFs) ZIF-8 and ZIF-67 were tested as solid catalyst in the transformation of hexoses (glucose, fructose) and sucrose into methyl lactate in a methanol medium. The results of the sugar conversion with all these catalysts are summarized in Table 1. Other MOF based catalysts (HKUST-1 (Cu), MIL-53(Al) and MIL-101(Cr)) with good initial expectations gave rise to methyl lactate yields below 5 %, thus they were discarded from the in-depth study.

**Table 1. Catalytic results obtained for sugar conversion with different catalysts. Showing yields to methyl lactate (ML), pyruvaldehyde dimethyl acetal (PADA), 1,1,2,2-tetramethoxypropane (TMP) and non-identified products (n.i.p.). Error of these values are shown in Table S1.**

Entry	Catalyst	Substrate	T <sup>a</sup> (°C)	Yields (%)				Total yield (%)	Sugar conversion (%)
				ML	PADA	TMP	n.i.p.		
1	Blank	Sucrose	160	1.4	2.5	0.1	4.3	8.3	88.6
2	Blank	Glucose	160	1.1	2.5	-	6.0	9.6	87.3
3	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Sucrose	160	22.1	1.4	0.6	3.5	27.6	98.7
4	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Glucose	160	19.6	2.4	0.3	2.5	24.8	94.5
5	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Sucrose	160	25.9	0.2	0.1	1.2	27.4	> 99.1
6	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Glucose	160	23.0	-	-	1.2	24.2	98.5
7	ZIF-8	Sucrose	160	34.8	1.9	0.4	3.3	40.4	> 99.1
8	ZIF-8 <sup>a</sup>	Glucose	160	19.8	0.8	0.1	2.0	22.7	98.1
9	ZIF-8 <sup>a</sup>	Fructose	160	10.5	-	-	1.5	12.0	97.9
10	ZIF-67	Sucrose	160	19.1	0.1	0.1	2.4	21.7	65.9
11	ZIF-67	Glucose	160	10.4	0.2	0.1	2.0	12.7	78.5
12	ZIF-8	Sucrose	120	6.1	0.1	0.2	9.1	15.5	75.4
13	ZIF-8	Sucrose	80	2.2	-	-	7.2	9.4	74.9

11

12 **Reaction conditions: 24 h, 160 mg of catalyst and 225 mg of sugar. <sup>a</sup> Reaction time: 20 h.**

13

1 First of all, blank experiments without catalysts were carried out. Although high  
2 conversions of sugar were obtained in these experiments, methyl lactate (ML) was  
3 detected in small quantity, giving rise to  $1.4 \pm 0.9$  % and  $1.1 \pm 0.7$  % (error derived  
4 from 3 different experiments) for sucrose and glucose, respectively (Entries 1, 2; Table  
5 1). Nevertheless, Holm et al. found that sucrose and glucose gave methyl lactate yields  
6 with no catalyst of 6 % and 5 %, respectively [14].

7 Experiments with  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were carried out in order  
8 to compare the performance of the metal salts with those of the corresponding ZIFs  
9 (Entries 3 – 6; Table 1). In these experiments, the same conditions and amount of metal  
10 as for the corresponding ZIF were used. ZIF-8 shows better results than its precursor  
11 metal salt. About 10 % more yield of methyl lactate was achieved with sucrose as  
12 substrate, 22.1 % with the salt and 34.8 % for the solid catalyst ZIF-8. Thus, the best  
13 performance of the heterogeneous catalysis is obvious and it will be of interest to study  
14 this MOF as catalyst in the conversion of sugars in greater depth. In contrast, the ZIF-67  
15 catalyst did not improve on the results of the corresponding Co salt.

16 The sugar (sucrose, glucose) conversion using Co and Zn salt are similar.  
17 However, comparing the performance of ZIF-8 and ZIF-67 (Entries 7 – 11; Table 1), it  
18 can be seen that the methyl lactate yield obtained from sucrose at 160 °C in 24 h using  
19 ZIF-67 as catalyst was only 19.1 %. Nevertheless, the methyl lactate yield reached  
20 34.8% with ZIF-8, in the same reaction conditions. Although both solids had the same  
21 sodalite structure (see Fig. 1), in this reaction ZIF-67 showed lower catalytic activity  
22 than ZIF-8. There are two factors that can explain this behavior: the crystal size and the  
23 acidity of the metal sites. Firstly, the crystal size of ZIF-67 is larger (about 1  $\mu\text{m}$ ) than  
24 that of ZIF-8 (100-150 nm); thus, in smaller crystals the accessibility of reactants to the  
25 active sites is improved (see Fig. 3). Secondly, Lewis acid sites are needed for carrying

1 out the conversion of sugars to methyl lactate [14] and its presence determined by  
2 pyridine adsorption has been reported in the literature in ZIF-8 [62]. In fact, ZIF-8 has  
3 stronger acid sites while the catalytic sites of ZIF-67 are moderately acid, according to  
4 measurements in the literature using NH<sub>3</sub> and CO<sub>2</sub> temperature-programmed desorption  
5 [57].

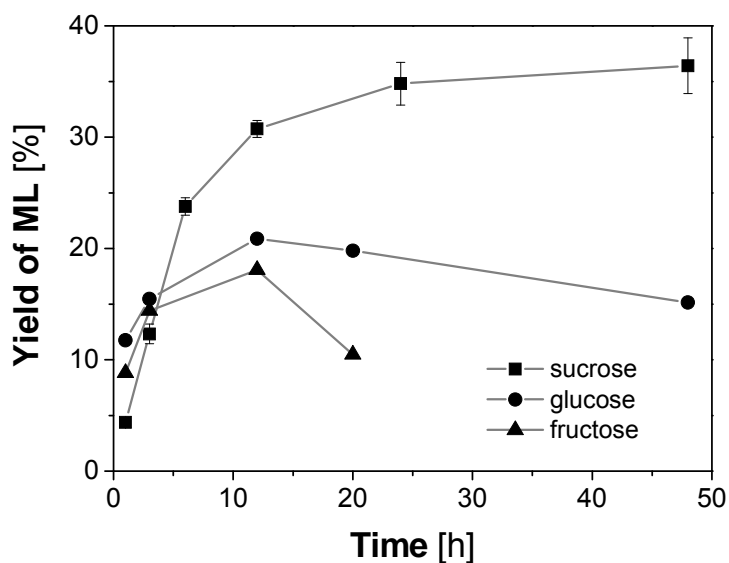
6 Some by-products were detected by GC-MS such as pyruvaldehyde dimethyl  
7 acetal (PADA), 1,1,2,2-tetramethoxypropane (TMP) and others which were not  
8 identified. Their yields are also shown in Table 1. However, the yields to these by-  
9 products were quite low, so the catalysts presented high yield towards methyl lactate.

10 In the case of the catalyst ZIF-8, the sucrose reaction was studied at 80, 120 and  
11 160 °C (Entries 7, 12, 13; Table 1), finding 160 °C as the best temperature from the  
12 point of view of the yield to methyl lactate. Temperatures of 80 and 120 °C were found  
13 to be too low for the transformation of sucrose into methyl lactate, showing yields  
14 below 10 % (Entries 12, 13; Table 1). In addition, sucrose conversions at 80 and 120 °C  
15 were about 75 %, while at 160 °C it was near 100%. A high reaction temperature was  
16 likely to be favorable not only for a complete reaction, but also for yield towards methyl  
17 lactate.

18 Fig. 4 shows the performance of the catalyst ZIF-8 with different sugars  
19 (sucrose, glucose and fructose) as a function of reaction time. At short times (1 h),  
20 glucose and fructose (initial reaction rates 191 and 143 g ML (g catalyst·h)<sup>-1</sup>,  
21 respectively) are more reactive and gave a higher ML yield than sucrose (initial reaction  
22 rates 75 g ML (g catalyst·h)<sup>-1</sup>). At longer times, sucrose as substrate gave the highest  
23 methyl lactate yield. Ca. 35.0 % of methyl lactate yield was reached at 24 h using  
24 sucrose, increasing only up to 36.4 % after 48 h. This may be due to the thermostability

1 and hydrolytic resistance of the disaccharide and the slow release of hexoses from  
2 sucrose in solution which prevents unwanted side reactions with the more reactive  
3 glucose and fructose [27]. As a consequence in contrast to sucrose, the hexoses had the  
4 best performance at 12 h of reaction, reaching methyl lactate yields of 18.1 % and 20.9  
5 % from fructose and glucose, respectively. Using ZIF-67 as catalyst (Table 1) after 20 h  
6 of reaction, the methyl lactate yield was bigger for sucrose than for glucose, similar to  
7 when the ZIF-8 is used as a catalyst.

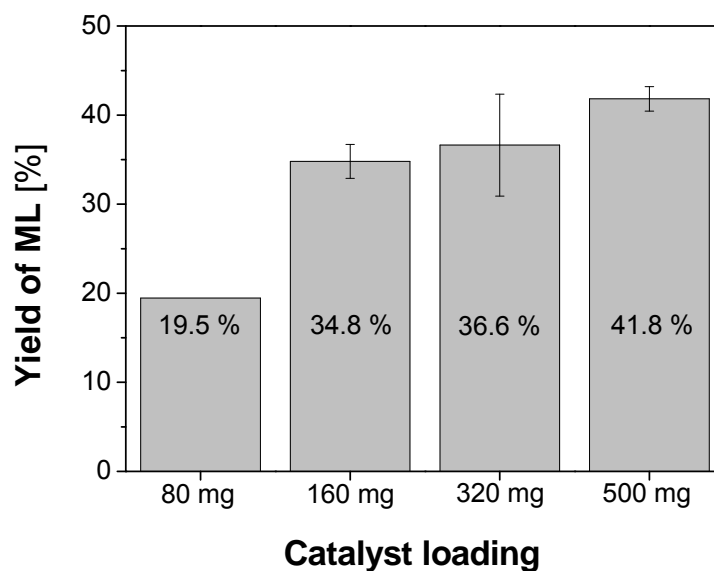
8       It is worth mentioning that the carbon balance, taking into account all the products  
9 detected and the sugar conversion, did not reach 100 %. This was probably caused by  
10 the production of some polymerization products, humic acids or other carbonaceous  
11 compounds which were not detected by gas chromatography. This kind of compounds  
12 of unwanted reactions is, certainly, formed in greater amounts in glucose and fructose  
13 than sucrose and at longer times it may be responsible to react with methyl lactate  
14 reducing their yield.



1  
 2 **Fig. 4. Yield of methyl lactate (ML) obtained over ZIF-8 using different sugars as reactants. Error**  
 3 **bars in the case of sucrose derived from at least 4 different experiments (Reaction conditions: 160**  
 4 **°C, 160 mg of catalyst and 225 mg of sugar). Profiles of concentration of ML and other products are**  
 5 **shown in Fig. S5.**

6  
 7 The influence of the amount of catalyst present in the reaction mixture was also  
 8 studied (80-500 mg) and the results are presented in Fig. 5. The tests were carried out at  
 9 160 °C for 24 h and sucrose was used as the carbohydrate feedstock. 160 mg can be  
 10 considered as the optimum value (methyl lactate yield ~35%), since with lower amounts  
 11 of catalyst only a 20 % methyl lactate yield was barely reached, while with double  
 12 (methyl lactate yield ~37%) or even with triple (methyl lactate yield ~42%) the amount  
 13 of catalyst the increase in the methyl lactate yield was less significant.





1  
2 **Fig. 5. Comparison of different amounts of ZIF-8 in the conversion of sucrose into methyl lactate**  
3 **(ML).Error bars derived from at least 3 different experiments. (Reaction conditions: 160 °C,24 h**  
4 **and 225 mg of sugar).**

5  
6 In a previous work, we proposed a possible reaction pathway for the  
7 transformation of glucose in the same conditions, but with silicate (MCM-41, JDF-L1,  
8 AM-4, UZAR-S1, UZAR-S2) based catalysts, which may be applicable to this case  
9 [21]. Different reactions take place in the conversion of sugars to methyl lactate (see  
10 Fig. S1). The first step when using polysaccharides corresponds to their hydrolysis,  
11 producing sugars with less carbon content. In consequence, sucrose hydrolyzes forming  
12 glucose and fructose. Afterwards, the isomerization of glucose to fructose or vice versa  
13 occurs. Then the retro-aldol reaction of fructose gives rise to trioses, i.e. DHA  
14 (dihydroxyacetone) or GLY (glyceraldehyde), together with an isomerization step. The  
15 next steps involve the dehydration of the trioses, although there is no agreement as to  
16 whether DHA (ketose form) or GLY (aldose form) is the final dehydrate intermediate. It  
17 is thought that the reaction to methyl lactate could start from either of these precursors.

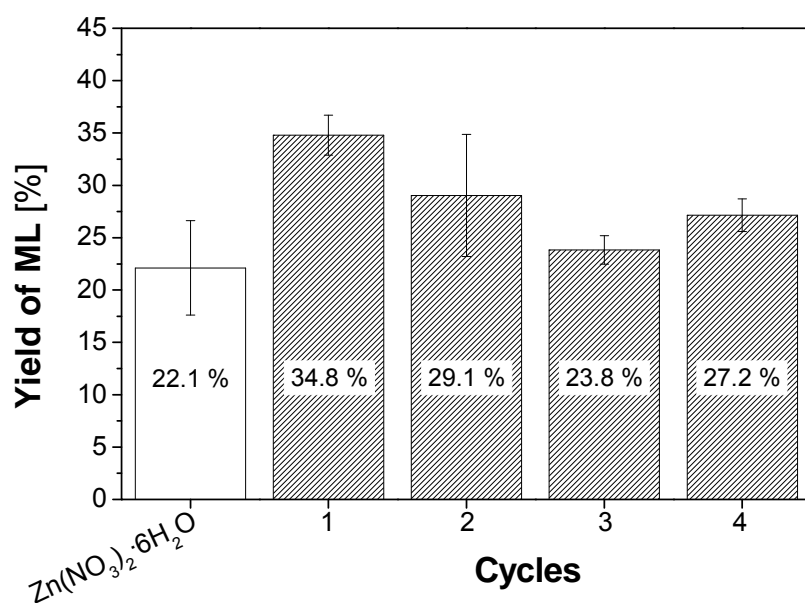
1 The dehydration reaction produces pyruvic aldehyde which is prone to a  
2 nucleophilic attack on its aldehyde carbonyl with an alcohol (methanol in this case), and  
3 the corresponding hemiacetal is formed. The last step is a 1,2-hydride shift, either the  
4 incorporation of another methanol molecule forming the pyruvaldehyde dimethyl acetal  
5 (PADA) or the isomerization into methyl lactate. The alkyl acetal can react with another  
6 methanol molecule and form 1,1,2,2-tetramethoxypropane (TMP).

7 It has been reported that Lewis acid sites play an important role in both  
8 isomerization steps and the 1,2-hydride shift. Besides, it should be noted that the retro-  
9 aldol step occurred from fructose; however, the same reaction could occur from glucose  
10 and generate some polymer architectures [5].

### 11 **3.3. Reuse of ZIF-8**

12 Given the high methyl lactate yield (35 %, Table 1), the reusability tests of ZIF-8  
13 were carried out using sucrose as substrate at 160 °C for 24 h with 160 mg of catalyst in  
14 each run. The performance of this catalyst in consecutive catalytic cycles was compared  
15 with that of Zn salt used in the synthesis of ZIF-8. For making the comparison as real as  
16 possible, the amount of salt used corresponded to the moles of Zn contained in 160 mg  
17 of ZIF-8 (Fig. 6). An activation step between runs was carried out because a  
18 thermogravimetric analysis (Fig. 7) showed that some compounds remained adsorbed  
19 (weight loss between 165 and 300 ° C) on the recovered ZIF-8 after the reaction  
20 process. The activation consisted of drying the recovered solid under vacuum at 190 °C  
21 for 12 h, being enough to remove the adsorbed compounds related to mentioned weight  
22 loss (see activated recovered solid in Fig. 7). It should be noted that after the first  
23 catalytic cycle for sucrose, that means in the second catalytic cycle, without activation  
24 the ML yield was 23.8%, while if the catalyst was activated the ML yield increased up

1 to 29.1%. Other alternatives for activation were studied, such as methanol washing and  
2 calcination at different temperatures, but none of them was as successful as vacuum  
3 drying either because the adsorbed compounds were not removed or because the ZIF-8  
4 structure was lost.

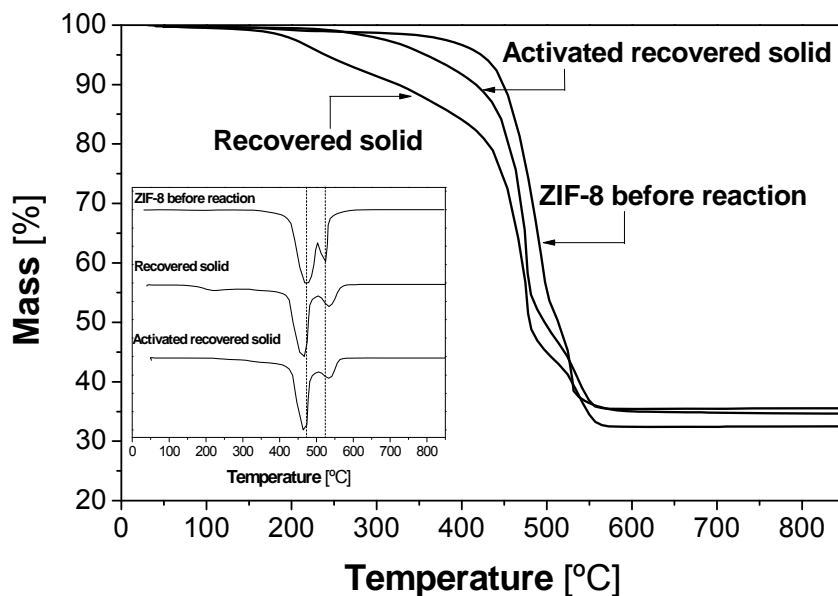


5

6 **Fig. 6. Reusability of ZIF-8 for the conversion of sucrose to methyl lactate (ML).**

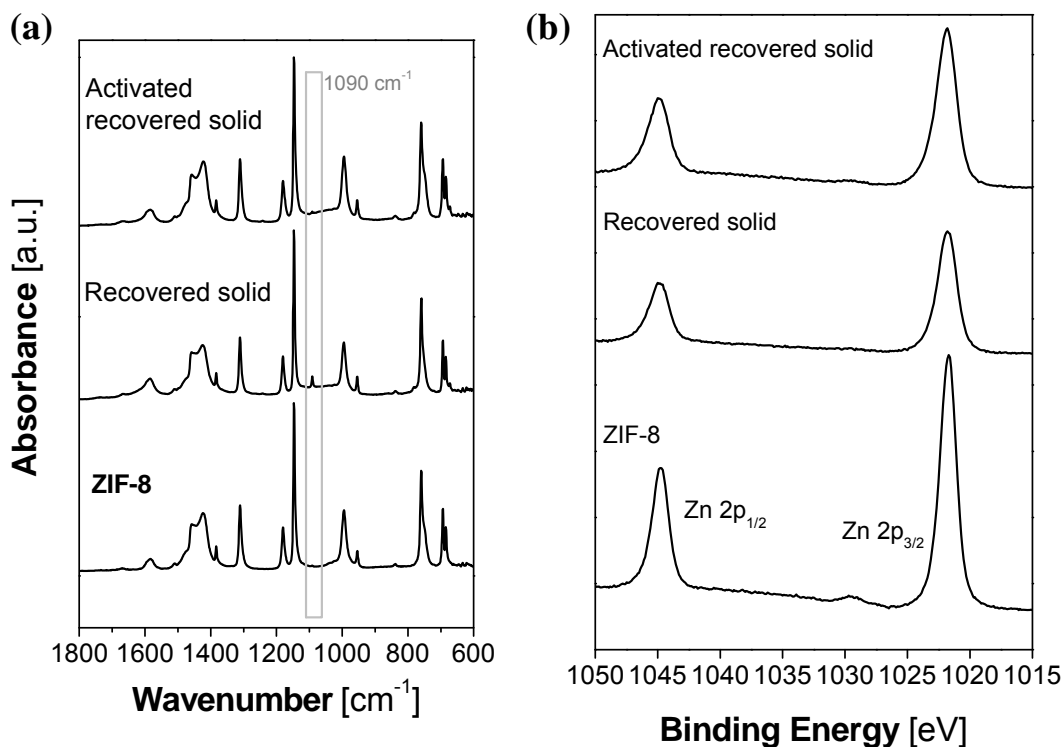
7 **(Reaction conditions: 160 °C, 24 h, 160 mg of catalyst and 225 mg of sugar.**

8



1  
2 **Fig. 7. TGA curves of catalysts: ZIF-8 before reaction, recovered solid after reaction and activated**  
3 **recovered solid by drying under vacuum. The inset shows the corresponding derivatives.**

4  
5 Characterization by ATR spectroscopy was used as a complement to the  
6 thermogravimetric analysis and to identify the nature of the adsorbed compounds. Fig.  
7 8a depicts an IR peak at  $1090\text{ cm}^{-1}$  which indicated the presence of a C-C bond in the  
8 recovered solid that did not exist in fresh ZIF-8. This suggests that some carbonaceous  
9 species were adsorbed in the catalyst after reaction. By means of activation this peak  
10 disappeared, which confirmed that most of the compounds were successfully removed.



1  
2 **Fig. 8. ZIF-8 before reaction, recovered solid after reaction and activated recovered solid by drying**  
3 **under vacuum: (a) ATR spectra. (b) Zn 2p XPS spectra.**

4  
5 More information about the chemical structure of the recovered solid was  
6 achieved by XPS spectroscopy. The corresponding spectrum was compared with that of  
7 fresh ZIF-8. Binding energy related to Zn 2p (1021.7 eV) did not change for the two  
8 samples (see Fig. 8b) although there was a decrease in the intensity and peak  
9 broadening which is related to loss of crystallinity, as observed by XRD. The Zn 2p  
10 XPS shows the peak FWHM broadens post-reaction, indicative of the formation of a  
11 range of chemical environments in the spent catalyst. This deactivation is further  
12 evidenced by the change in N/Zn surface composition given in Table 2. Regarding the  
13 N/Zn ratio, fresh ZIF-8 was almost at the theoretical value, i.e. 4.0 corresponding to  
14 ZnN<sub>4</sub> tetrahedra in the ZIF-8 framework. After the catalytic reaction, the reduction of  
15 N/Zn at the surface was significant (2.0) and could be related to some ligand

1 degradation. The C/N atomic relation increased, related to the above-mentioned  
2 adsorbed compounds. Finally, the C/N ratio decreased upon reactivation, consistent  
3 with the cleaning of the catalyst surface.

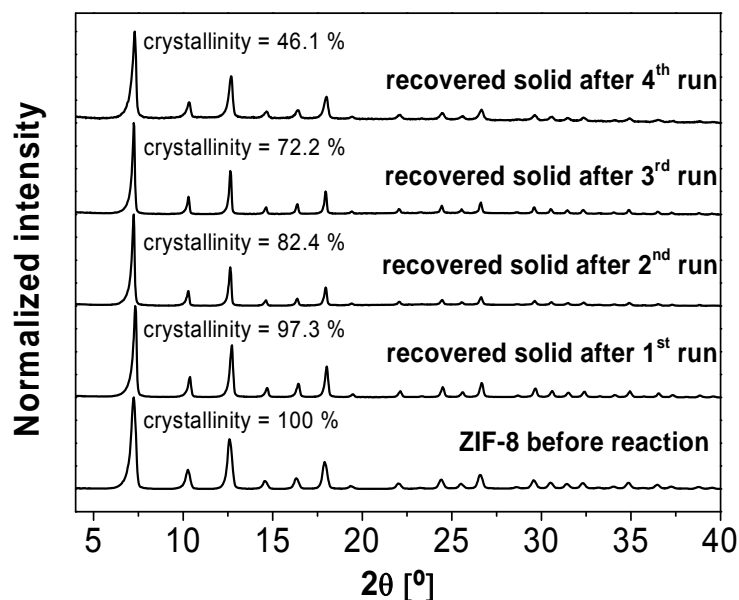
4 **Table 2. XPS results, atomic relation between elements for ZIF-8 before reaction, recovered solid**  
5 **after reaction and activated recovered solid by drying under vacuum.**

6	7	8	9
Sample	C/N	N/Zn	
ZIF-8	2.3	3.9	
Recovered solid	4.6	2.0	
Activated recovered solid	3.5	2.6	

11 The ZIF-8 catalyst could be reused for at least 4 cycles with a loss of activity  
12 from 34.8 % to 27.2 %, as shown in Fig. 6. The methyl lactate yield in the first run was  
13 over 35 %, while in the subsequent runs it decreased to about 25 %. This decrease is  
14 consistent with the adsorption of some compounds which could not be removed during  
15 the reaction itself. The degradation of the ZIF-8 structure, probably more intense at the  
16 particle surface, cannot be discarded since the textural properties of the catalyst were  
17 also affected (see Table 3).

18 Other characterization techniques were applied to the catalysts after the catalytic  
19 runs. There was no difference in terms of XRD patterns in the ZIF-8 before reaction and  
20 after the catalytic cycles, as can be observed in Fig. 9. This confirms that the structure in  
21 bulk is maintained during the catalytic tests. However, the intensity of the first peak  
22 (around 7.2°) decreased as the number of runs increased (from about 47,000 to 20,000  
23 counts for the fresh and fourth cycle catalysts, respectively). In Fig. 9 the percentage of  
24 crystallinity is presented, it was calculated respect to the peak at  $2\cdot\theta=7.2^\circ$ , the catalyst

1 before reaction corresponding to 100%. Therefore, a reduction in crystallinity is more  
2 than evident, in agreement with the previous XPS characterization which suggested  
3 some surface changes.



4

5 **Fig. 9. XRD patterns of ZIF-8 before the reaction (fresh catalyst) and recovered solids after the**  
6 **various catalytic cycles. Including percentage of crystallinity, referred to catalyst before reaction.**

7

8 After each reaction cycle, it was measured N/Zn and C/Zn atomic ratios by EDX  
9 (Table S2) in activated recovered solid. By increasing the number of reaction cycles,  
10 there is a decrease of the N/Zn atomic ratio which would agree with the loss of  
11 crystallinity and the C/Zn ratio decreases slightly indicating that Zn scarcely leaches.

12 Table 3 summarizes the textural properties of fresh ZIF-8 and used ZIF-8 after  
13 four successive catalytic runs. The BET specific surface area was reduced after each  
14 cycle from the initial value of 1,391 to 757 m<sup>2</sup> g<sup>-1</sup> after the fourth run. A parallel  
15 decrease in pore volume also occurred throughout the cycles (from 0.66 to 0.48 cm<sup>3</sup>·g<sup>-1</sup>  
16 <sup>1</sup>). These changes are in line with the previous TGA, FTIR and XPS results, suggesting

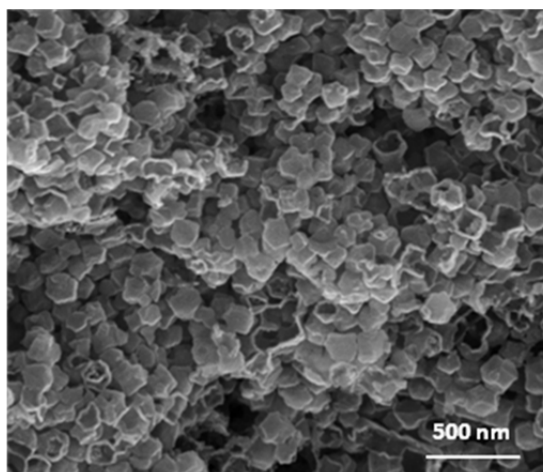
1 the adsorption of some compounds on the MOF surface. Besides, some structure  
 2 collapse from the particle surface to its interior could be possible, even though the XRD  
 3 patterns always correspond to the sodalite type structure of ZIF-8 (Fig. 9). SEM images  
 4 for activated recovered solid after the first and second reaction cycles (Fig. S6) do not  
 5 show apparent changes in the morphology, but the edges are rounded after the third  
 6 reaction cycle (Fig. S6). After the fourth reaction cycle, Fig. 10 shows how the ZIF-8  
 7 crystals exhibited some hollow particles, even though the typical rhombic dodecahedron  
 8 shape was maintained. These hollows suggest dissolution which may contribute,  
 9 together with the above-mentioned adsorption on the catalyst surface, to the loss of  
 10 activity at least up to the third cycle (see the methyl lactate yield in Fig. 6). However,  
 11 the increase in activity from the third to the fourth cycle could be due to these hollows  
 12 allowing better access to the active sites.

13 **Table 3. Textural properties of the catalyst after reaction cycles. (BET specific surface area and**  
 14 **pore volume measured at  $P/P^0 = 0.97$  by nitrogen adsorption)**

<b>Cycle</b>	<b>BET Area (<math>\text{m}^2 \text{g}^{-1}</math>)</b>	<b>Pore Volume (<math>\text{cm}^3 \text{g}^{-1}</math>)</b>
Fresh	$1,391 \pm 26$	0.66
1	$1,102 \pm 21$	0.65
2	$1,076 \pm 19$	0.62
3	$869 \pm 15$	0.54
4	$757 \pm 11$	0.48

15





1  
2 **Fig 10. SEM image of activated ZIF-8 after fourth run of catalytic reaction.**

3  
4 Finally, even if the highest yield to methyl lactate from sucrose (around 42 %) reached here is below the yields reported for Sn-Beta zeolite (64 %) [14] and Sn-MCM-  
5 41 (43 %)[21], the present work is not only interesting because of the relatively good  
6 performance of the ZIFs but also because new opportunities in which MOFs may have  
7 useful applications in biorefinery emerging processes.  
8

#### 9 **4. Conclusions**

10 ZIFs were used for the first time in the transformation of sugars to lactic acid  
11 derivatives, such as methyl lactate, with high conversion and yield. ZIF-8 and ZIF-67  
12 were synthesized following a previously developed method. Although both solids had  
13 the same sodalite type structure, their behavior as catalysts in sugar conversion was  
14 different. ZIF-67 was found not to be efficient for the process; however, ZIF-8 gave a  
15 better catalytic performance than its corresponding metal salt. Thus ZIF-8 was found to  
16 be an active and selective catalyst for the conversion of sugars into methyl lactate. The  
17 optimum reaction conditions were 24 h at 160 °C using 160 mg of catalyst. Although  
18 methyl lactate was not the only product detected, a high yield was observed.

1 The use of sucrose as substrate provided the best catalytic results with ZIF-8.  
2 Besides, ZIF-8 could be reused for at least four cycles with methyl lactate yield drop  
3 from 34.8% in the first cycle to 27.2 % in the fourth cycle.. An activation process of the  
4 catalyst was needed between runs due to some compounds being adsorbed during the  
5 reaction and some chemical, textural and morphological effects occurring, as evidenced  
6 by the characterization carried out. Finally, it should be noted that MOFs, with their  
7 highly desirable and tunable structural, textural, morphological and compositional  
8 properties, would be attractive materials for use as catalysts in the heterogenization  
9 reaction of sugars to produce methyl lactate, and similar processes.

## 10 **5. Acknowledgments**

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13 Government (DGA, T05) is gratefully acknowledged. The authors would like to  
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15 la Investigación-SAI and the Laboratorio de Microscopías Avanzadas (LMA) at INA.

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- 3

1 **SUPPORTING INFORMATION**

2 **Chemocatalysis of sugars to produce lactic acid derivatives on**  
3 **zeolitic imidazolate frameworks**

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11

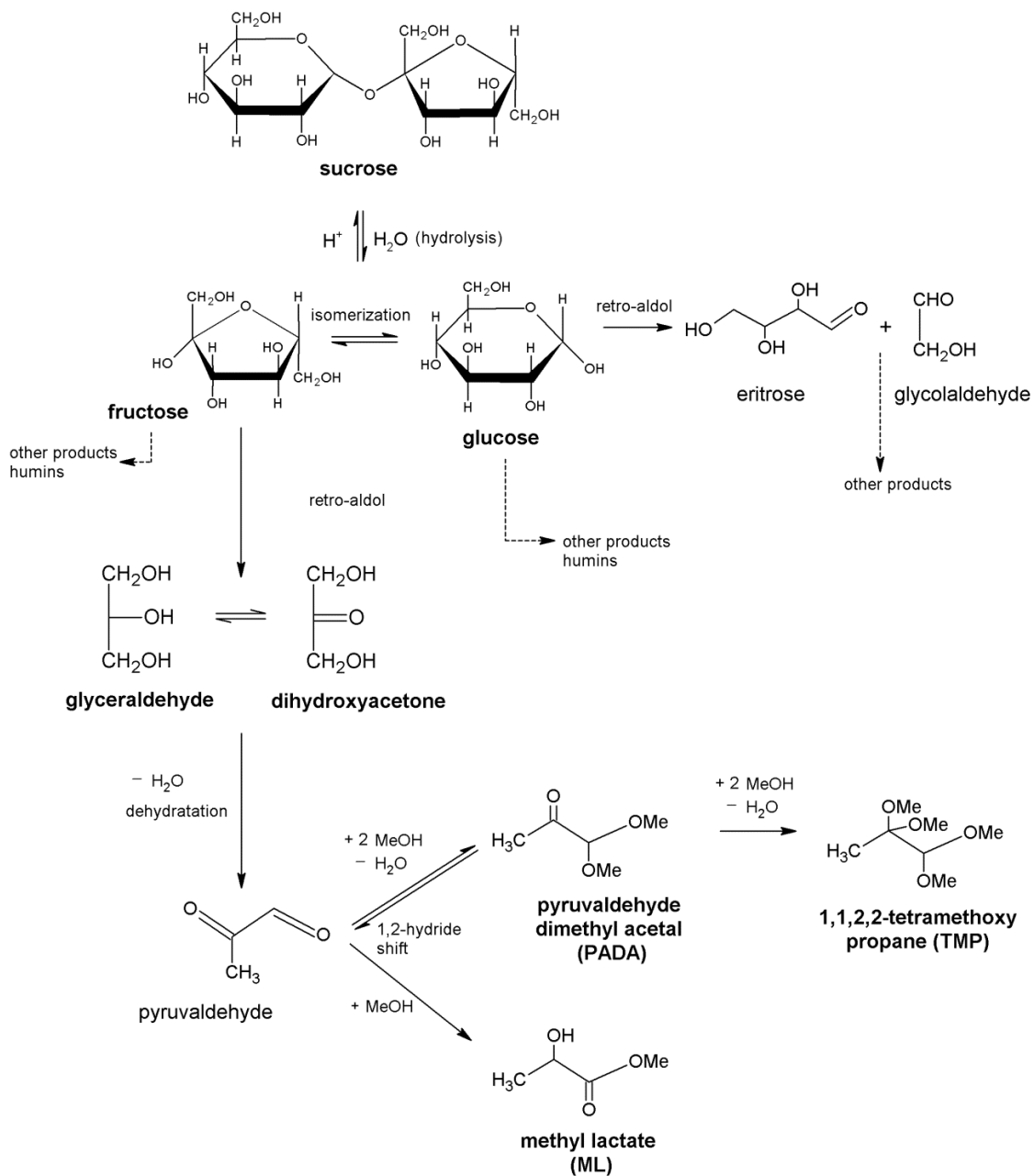
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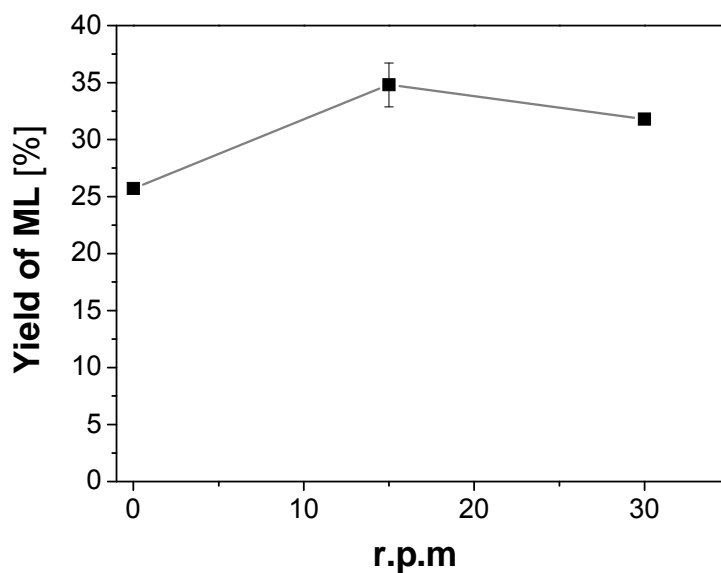
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**Figure S1. Possible pathway for the conversion of sucrose to methyl lactate using ZIF-8 based on mechanism on references [1-2].**



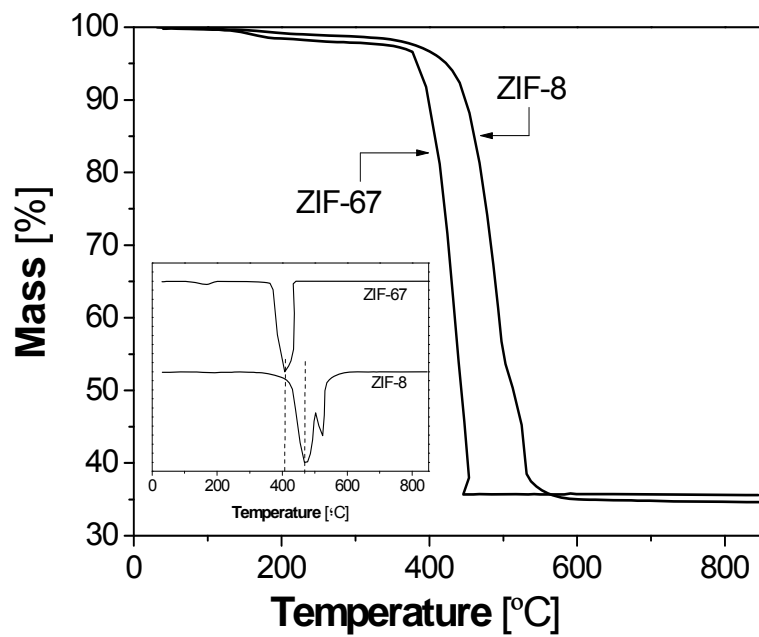
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Figure S2. Picture of the rotatory oven used in the catalytic conversion of sugars reaction.



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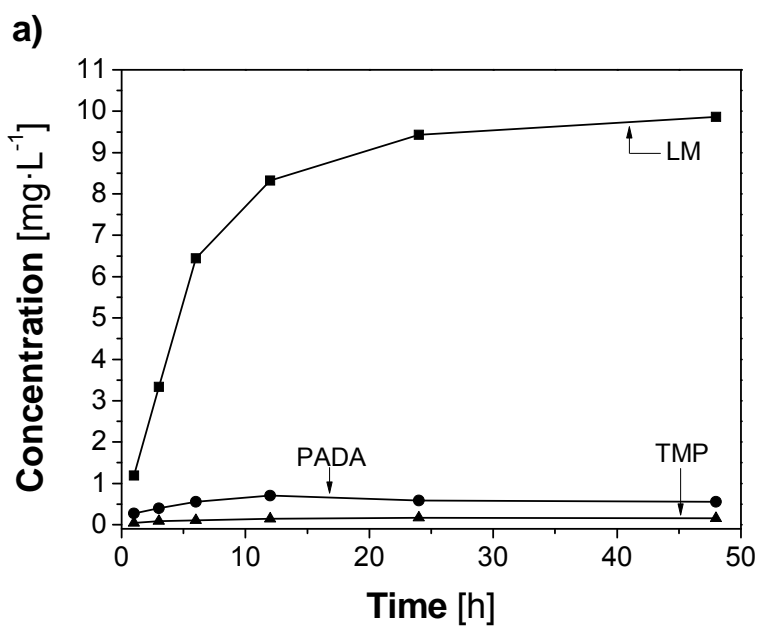
Figure S3. Yield of methyl lactate (ML) obtained over ZIF-8 using different revolutions per minute (r.p.m) in the rotatory oven. (Reaction conditions: 160 °C, 160 mg of catalyst and 225 mg of sucrose).



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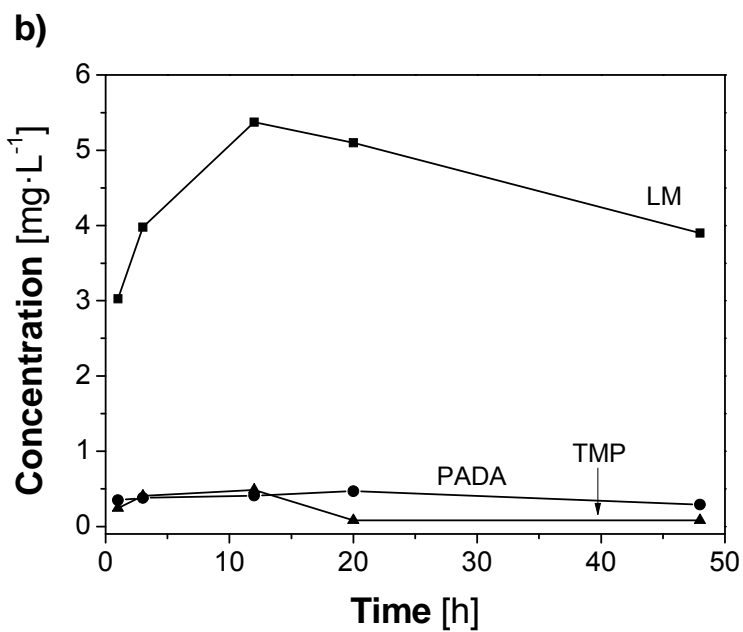
2 **Figure S4. TGA curves and derivatives of ‘as-synthesized’ ZIF-8 and ZIF-67.**

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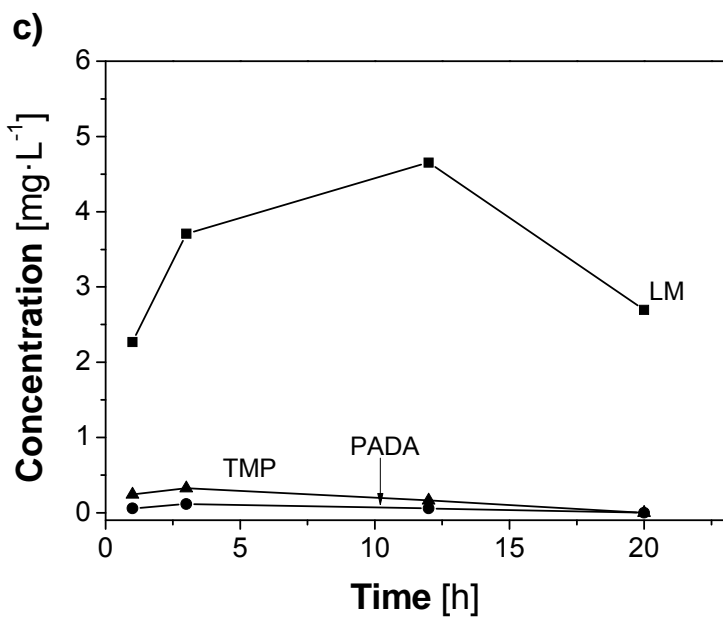


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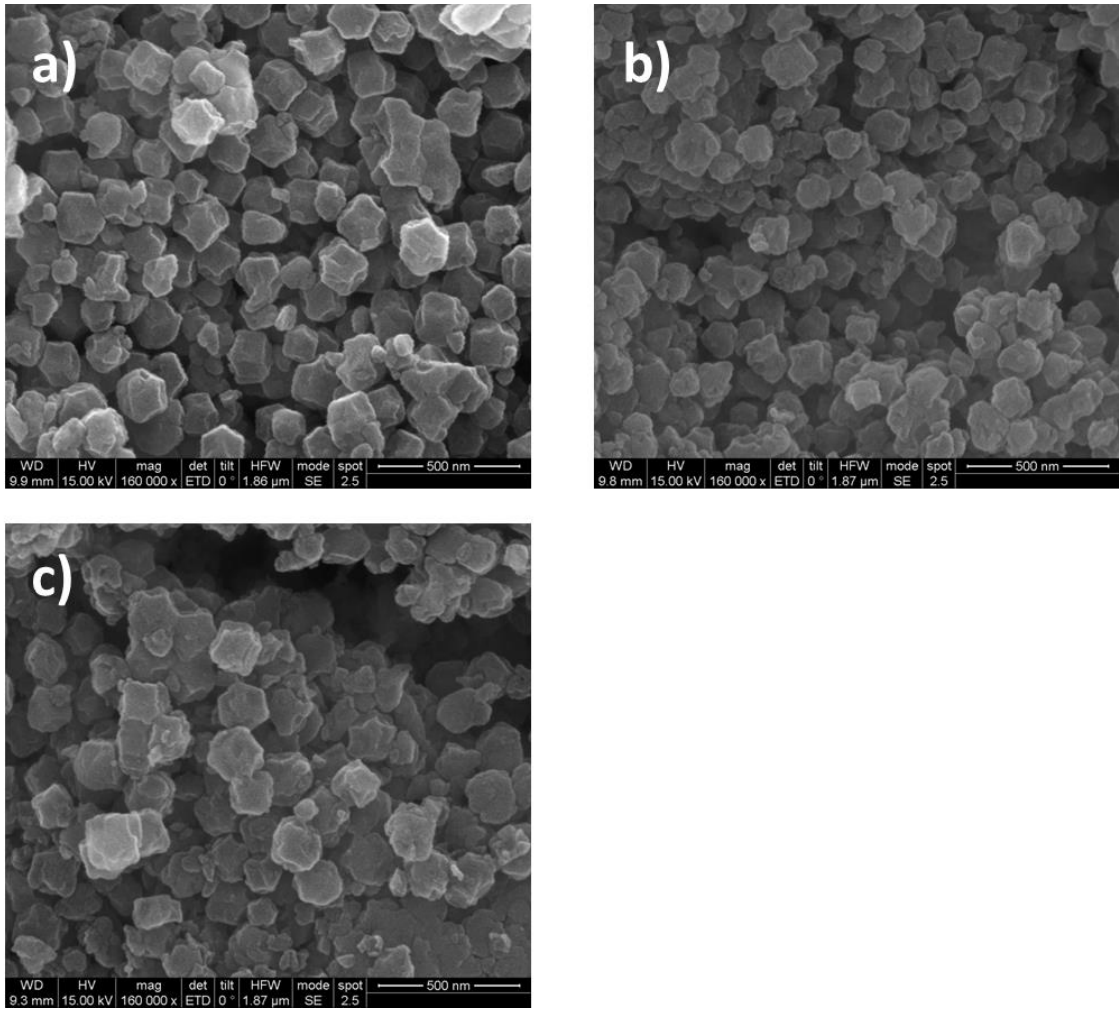
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**Figure S5. Concentration profile of analyzed products obtained over ZIF-8 using different sugars as reactants: a) Sucrose. b) Glucose. c) Fructose. (Reaction conditions: 160 °C, 160 mg of catalyst and 225 mg of sugar).**

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**Figure S6. SEM images for activated recovered solid after each run: (a) recovered solid after 1<sup>st</sup> run, (b) recovered solid after 2<sup>nd</sup> run, (c) recovered solid after 3<sup>rd</sup> run.**

1 Table S1. Errors for yield values obtained for sugar transformation with different catalysts. Methyl  
 2 lactate (ML), pyruvaldehyde dimethyl acetal (PADA), 1,1,2,2-tetramethoxypropane (TMP) and  
 3 non-identified products (n.i.p.). Errors entries 1-7, 10, 11 from different experiments (at least 3).  
 4 Errors entries 8, 9, 12, 13 analysis error. Reaction conditions: 24 h, 160 mg of catalyst and 225 mg  
 5 of sugar. <sup>a</sup>Reaction time: 20 h.

Entry	Catalyst	Substrate	Yields (%)			
			ML	PADA	TMP	n.i.p.
1	Blank	Sucrose	1.4 ± 0.9	2.5 ± 1.4	0.1 ± 0.04	4.3 ± 1.3
2	Blank	Glucose	1.1 ± 0.7	2.5 ± 1.2	-	6.0 ± 1.7
3	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Sucrose	22.1 ± 4.5	1.4 ± 1.1	0.6 ± 0.05	3.5 ± 1.2
4	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Glucose	19.6 ± 3.6	2.4 ± 1.5	0.3 ± 0.01	2.5 ± 1.3
5	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Sucrose	25.9 ± 2.3	0.2 ± 0.01	0.1 ± 0.02	1.2 ± 0.7
6	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O <sup>a</sup>	Glucose	23.0 ± 2.1	-	-	1.2 ± 0.9
7	ZIF-8	Sucrose	34.8 ± 1.9	1.9 ± 1.1	0.4 ± 0.02	3.3 ± 1.2
8	ZIF-8 <sup>a</sup>	Glucose	19.8 ± 2.6	0.8 ± 0.1	0.1 ± 0.03	2.0 ± 1.5
9	ZIF-8 <sup>a</sup>	Fructose	10.5 ± 2.2	-	-	1.5 ± 1.2
10	ZIF-67	Sucrose	19.1 ± 2.3	0.1 ± 0.03	0.1 ± 0.01	2.4 ± 1.8
11	ZIF-67	Glucose	10.4 ± 1.6	0.2 ± 0.01	0.1 ± 0.02	2.0 ± 1.2
12	ZIF-8	Sucrose	6.1 ± 0.2	0.1 ± 0.04	0.2 ± 0.05	9.1 ± 3.3
13	ZIF-8	Sucrose	2.2 ± 0.3	-	-	7.2 ± 4.6

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 11 Table S2. Energy Dispersive X-Ray (EDX) Analysis. This system is an attachment to Scanning  
 12 Electron Microscopy (SEM).

Sample	Atomic ratio	
	N/Zn	C/Zn
ZIF-8	4.4	10.5
Activated recovered solid after 1 <sup>st</sup> run	3.9	10.9
Activated recovered solid after 2 <sup>nd</sup> run	2.7	10.1
Activated recovered solid after 3 <sup>rd</sup> run	2.3	8.3
Activated recovered solid after 4 <sup>th</sup> run	1.1	8.4

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